Polarized light emission by deposition of aligned semiconductor nanorods

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ABSTRACT

The ability to control the position and orientation of nanorods in a device is interesting both from a scientific and a technological point of view. Because semiconductor nanorods exhibit anisotropic absorption, and spontaneous and stimulated emission, aligning individual NRs to a preferred axis is attractive for many applications in photonics such as solar cells, light-emitting devices, optical sensors, switches, etc. Electric-field-driven deposition from colloidal suspensions has proven to be an efficient method for the controlled positioning and alignment of anisotropic particles. In this work, we present a novel technique for the homogeneous deposition and alignment of CdSe/CdS NRs on a glass substrate patterned with transparent indium tin oxide interdigitated electrodes, with a spacing of a few micrometers. This method is based on applying a strong AC electric field over the electrodes during a dip-coating procedure and subsequent evaporation of the solvent. The reproducible and homogeneous deposition on large substrates is required for large size applications such as solar cells or OLEDs. The accumulation, alignment, and polarized fluorescence of the nanorods as a function of the electrical field during deposition are investigated. A preferential alignment with an order parameter of 0.92 has been achieved.

Keywords: Polarization, alignment, semiconductor, Nano rod, deposition, emission.

1. INTRODUCTION

Begin Controlling the position and orientation of nanorods (NRs) in a device is desirable [1-5]. In particular, an important property of NRs is their anisotropic absorption, and spontaneous and stimulated emission. NRs emit linearly polarized light along their long axis [6-9]. Hence aligning individual NRs to a preferred axis is interesting for many applications in photonics such as photovoltaic cells, photodetectors, OLEDs, optical sensors, etc [10-14].

Significant techniques for aligning NRs have been researched recently. Talapin *et al*.[4] demonstrate the self-organization of CdSe nanorods into nematic, smectic, and crystalline solids. Radial fluid flow with spin coating and drying lyotropic phase [1, 15], slow solvent evaporation at a liquid-solid-air interface [2, 13], coffee stain evaporation dynamic [14, 16, 17], or external electric fields [18], are some other techniques which are applied to align the NRs. Among them, aligned deposition of anisotropic particles from colloidal suspensions based on an applied alternating electric field is an efficient method for carbon nanotubes [19], nanowires [20], semiconductor [8, 11, 21-25], gold [18, 26] and NRs [27, 28]. Some of these techniques are summarized with their results in Table 1.

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Table 1. Comparison of methods for aligning NRs

Ref. Num.	NR	Substrate	Deposition method	Aligning method	Order parameter	Polarization ratio
[13]	CdSe/CdS	CBP	Contact printing	slow solvent evaporation method at the liquid-solid-air interface	-	0.34
[14]	CdSe/CdS	Glass	Drop casting	Coffee stain evaporation dynamics	-	-0.3
[29]	CdSe	ZnS/SiO_2	wet-chemical attachment	wet-chemical & epitaxial growth	-	0.54
[30]	CdSe/CdS	Glass	Spin coating	Mechanical Rubbing	-	0.49
[8]	CdSe/CdS	Si/SiO_2	Drop casting	DC field (2.5*10^7 V/m)	-	0.45
[22]	CdSe/CdS	Si_3N_4	Drop casting	DC field (2.8*10^7 V/m)	0.73	-
[26]	Gold NR	Silicon	Drop casting	AC field (2.4*10^6 V/m – 50kHz)	0.85	-
[28]	CdSe/CdS	Glass	Dip coating	AC field (1.8*10^7 V/m – 50kHz)	0.67	0.60
Our work	CdSe/CdS	Glass	Dip coating	AC field (2*10^7 V/m –1kHz)	0.92	0.58

The colloidal semiconductor NRs have an intrinsic dipole moment and a much higher dielectric constant than the apolar liquid. The NRs are subjected to random Brownian rotation. By applying an AC voltage with low frequency the NRs rotate to keep the permanent dipole moment parallel with the momentary field (dipolar torque). For a sufficiently strong electric field, the dielectric torque can also play a role to align the NRs [31]. However, the presence of the induced and permanent dipole moments, their strength, and their charge distribution, may vary for different NRs. In addition these physical quantities also depend on the specific properties (size, composition, crystal structure, etc.) and environment of the NRs.

In previous work [28], we presented a novel technique for the homogeneous deposition and efficient alignment of CdSe/CdS NRs on a glass substrate patterned with transparent indium tin oxide (ITO) interdigitated electrodes with a spacing of a few micrometers. This fast and versatile method is based on applying an electric field over the electrodes during a dip-coating procedure. This method is particularly suitable for the homogeneous deposition of aligned NRs on large and cheap transparent substrates as required for large scale applications such as solar cells or OLEDs.

In this work we improve the alignment of the NRs by applying higher electric fields. This is the case when the total electrostatic energy of a NR in an electric field ($p_0 E_{ext} + \frac{1}{2}\Delta p E_{ext}$) becomes larger than the thermal rotational energy $\frac{1}{2}kT$ [31]. In these formulas, E_{ext} is the applied electric field in the liquid and Δp is the induced dipole moment of the NR in the presence of the external electric field. The theory of applying electric field on NRs suspension is explained in previous work [31]. An alignment with order parameter of 0.92 is obtained with the new method. In addition, the accumulation, alignment, and polarized fluorescence of the NRs are also investigated and discussed here.

2. RESULTS AND DISCUSSION

The CdSe/CdS dot-in-rods with an average diameter of 4.8 nm and an average length of 51.5 nm are synthesized according to a procedure described in the literature[8]. The CdSe/CdS NRs are dispersed in chloroform and the solution is filtered with a 0.2 μm PTFE syringe filter. Figure 1a illustrates a transmission electron microscopy (TEM) image of the CdSe/CdS NRs. The structure of the NRs and their band structure with electron and hole wave function distributions in

the exited state are shown in figure 1b. Synthesis details, characterization techniques and optical characterization of the NRs can be found in previous work [28].

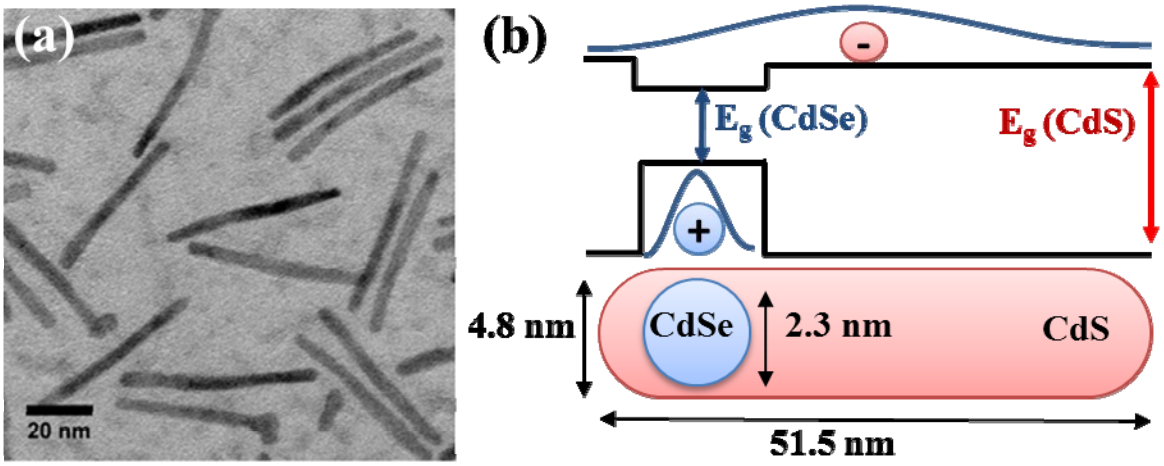

Figure 1. (a) TEM micrograph of the CdSe/CdS NRs. (b) Structure of the CdSe/CdS NRs and band structure with electron and hole wave function distributions in an exited state without the application of an electric field.

The substrate for the deposition of these NRs consists of a glass slide with an interdigitated finger pattern of ITO obtained by standard optical lithography. The thickness, length and width of the ITO fingers are 30 nm, 2600 μm and 12 μm respectively and the gap between to electrodes is 6 μm (figure 2).

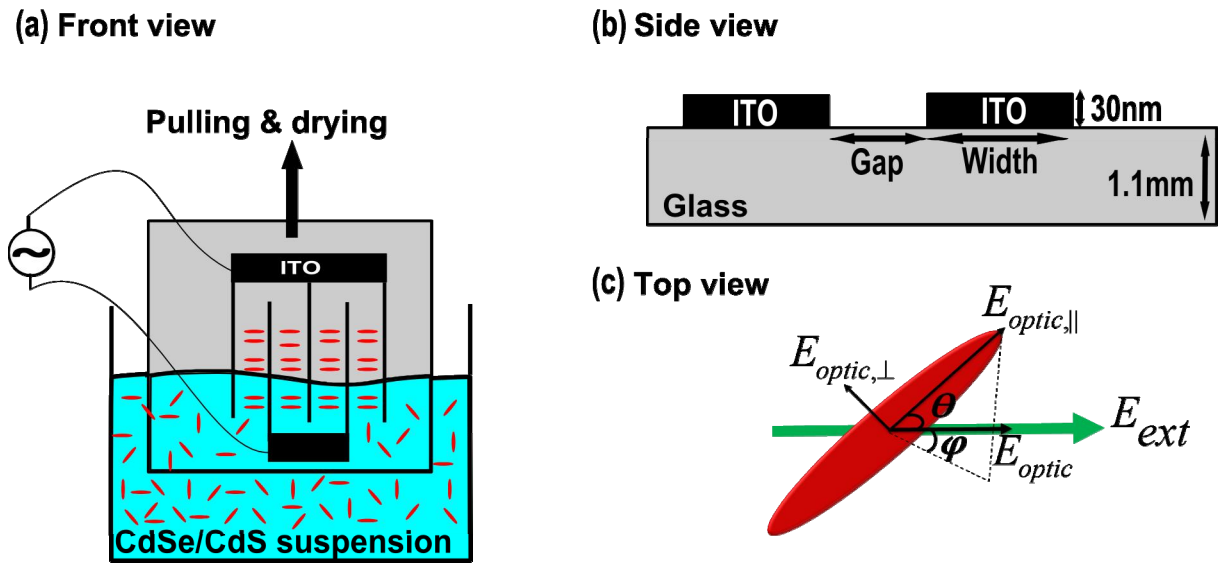

Figure 2. (a) A glass substrate with interdigitated ITO electrodes is pulled out of a NRs suspension in the presence of an alternating electric field. (b) The width of the ITO electrodes is 12 μm and the gap is 6 μm (not to scale). (c) The external electric field is perpendicular to the ITO lines, and θ is the angle between the electric field and the NR long axis.

A sketch of the experimental setup is shown in figure 2a and b. A function generator (TTi-TG315) and a voltage amplifier (FLC electronics-A800X) are used to apply an AC electric field up to 20 V/μm with 1 kHz frequency on the electrodes. The NRs are deposited by immersing the substrate vertically in a 10 nM CdSe/CdS solution. An alternating

voltage is applied while pulling the substrate out of the solution at a speed of 85.7 mm/minute. The voltage is switched off after the chloroform has dried (after a few seconds).

After deposition, the orientation of the NRs is investigated in detail by atomic force microscopy (AFM). The image data are analyzed by a computer program to determine the orientation of the NRs (figure 3). In a first step, the image is filtered with a threshold function to obtain a black and white image. In the second step, the image is filtered by a smoothing-Gaussian to attenuate the variations of the light intensity in the neighborhood of the NRs. In the third step, white regions that are surrounded by black pixels are identified. A maximum and minimum area for the white regions is set to avoid information from NR clusters and noise. The white regions in figure 3b are ascribed to individual NRs. Then the white regions are fitted to ellipses and the azimuth angles θ of the long axes are determined. Finally the histogram of the azimuth angles θ for the selected NRs is shown in figure 3c. The angle of the NRs is mostly between -10° to 10°, evidencing a clear preferential horizontal alignment (i.e. perpendicularly to the electrodes).

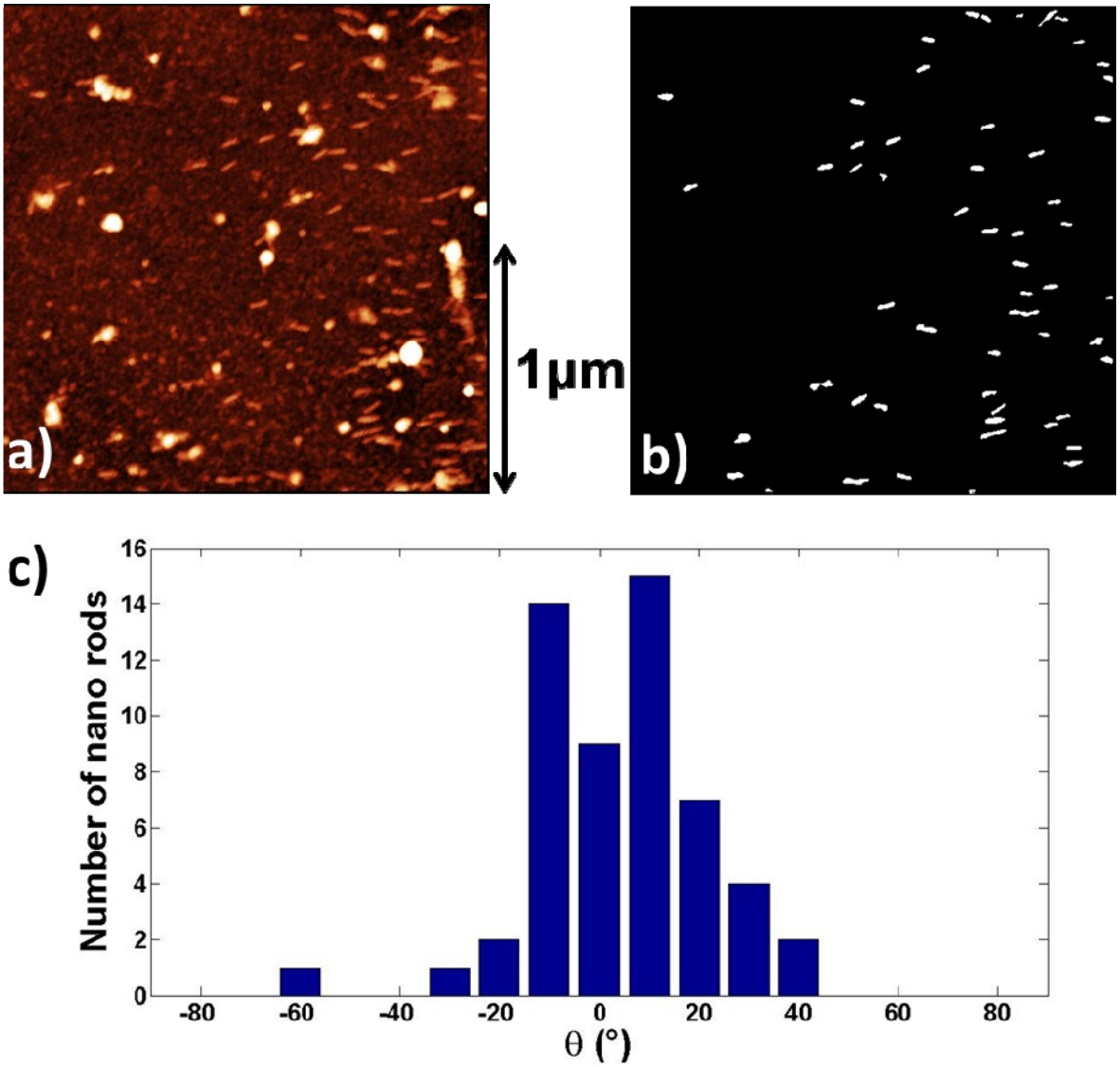

Figure 3. (a) AFM image of aligned NRs between electrodes deposited in the presence of an AC electric field with frequency 1 kHz and amplitude 20 V/µm. (b) Processed images to identify individual NRs. (c) Histogram of the azimuth angle (θ) of the NRs in image (b).

We use the azimuthal order parameter S, which is defined as $S = \langle 2\cos 2\theta - 1 \rangle$ to quantify the degree of NR alignment in the image. This expression accounts for the two-dimensional nature of the NR alignment and yields $S = 1$ in the case of perfect alignment and $S = 0$ in the case of random orientation[22, 26]. The obtained S is 0.92 which is higher than in previously cited works.

To observe the anisotropic emission of the deposited NRs, the layer is observed by fluorescence microscopy. The NRs are excited in the UV band (330-380 nm) of a Xenon lamp. The NRs emission is detected by an Andor CCD camera after passing a dichroic mirror and a linear polarizer (figure 4a). The fluorescence microscopy images in figure 4b are for the substrate with ITO in presence of an AC electric field (20 V/µm, 1 kHz) during dip coating. The polarizer (and the electric field of the transmitted light) is oriented perpendicular (figure 4b - right) or parallel (figure 4b - left) to the external electric field (and the alignment of the NRs). Figure 4b shows more NRs between the electrodes than on the electrodes, because the NRs are attracted by the strong electric field there. The strongest photoluminescence is observed when the polarizer is parallel to the alignment of the NRs ($\theta = 0$). This is in agreement with earlier polarization measurements on individual NRs [6] and aligned NR arrays [8, 9, 14].

The polarization of the fluorescence of the NRs is measured by detecting the intensity with a fluorescence microscope. The polarization ratio is given by: $\Pi_r = \left(I_{//} - I_{\perp}\right) / \left(I_{//} + I_{\perp}\right)$ [14] with $I_{//}$ and $I_{\perp}$ the photo luminescent intensity averaged over the gap between the electrodes, when the polarizer is oriented respectively parallel and perpendicular to the field that has been applied. The obtained polarization ratio from regions with aligned NRs is 0.58 whereas the fluorescence from regions with randomly oriented NRs yields a vanishing polarization ratio. The maximum polarization ratio for a single CdSe/CdS NR has been reported to be 0.75 [9]. The fact that the polarization ratio (~0.58) is lower than the order parameter (~0.92) may have several reasons: background fluorescence, loss of polarization due to scattering, unpolarized light from aggregates. It may also be due to the fact that the transition dipole moment of the emission process is not aligned with the NR long axis [28].

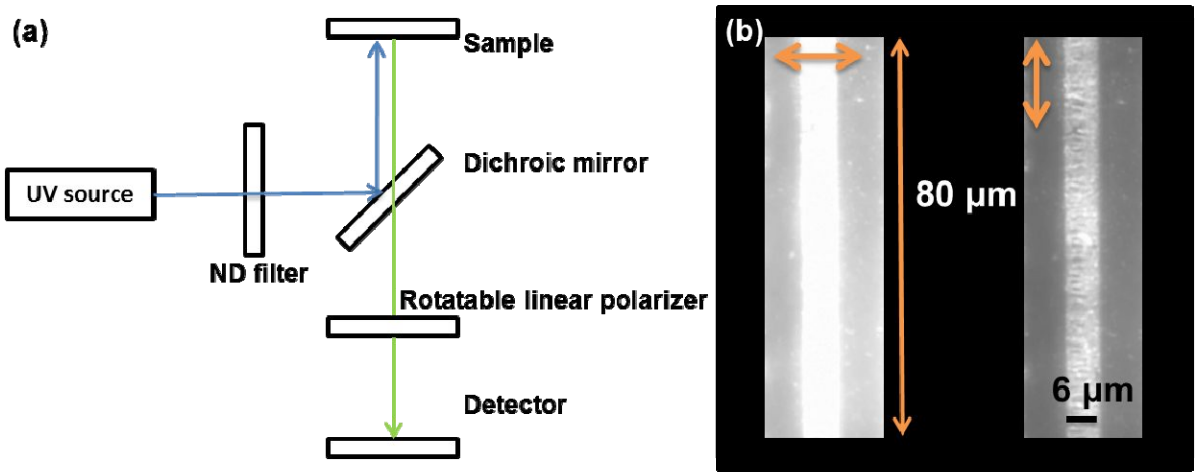

Figure 4. Fluorescence microscopy (a) set up and (b) images of a substrate (electrode gap of 6 µm as indicated by a scale bar) after dip-coating while the polarizer is oriented perpendicular (right) and parallel (left) to the alignment of the NRs.

3. CONCLUSION

A method for depositing aligned NRs on a substrate, based on an applied electric field is demonstrated. The deposition method is fast, easy, and can be applied on large substrates. An alignment with order parameter 0.92 is obtained which is higher than for previous methods reported in the literature. The fully aligned deposition of NRs has many applications such as back lights in LCDs, polarized OLEDs and polarization-selective detectors. We believe that this method can be extended to the deposition or printing of all kinds of aligned anisotropic particles.

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